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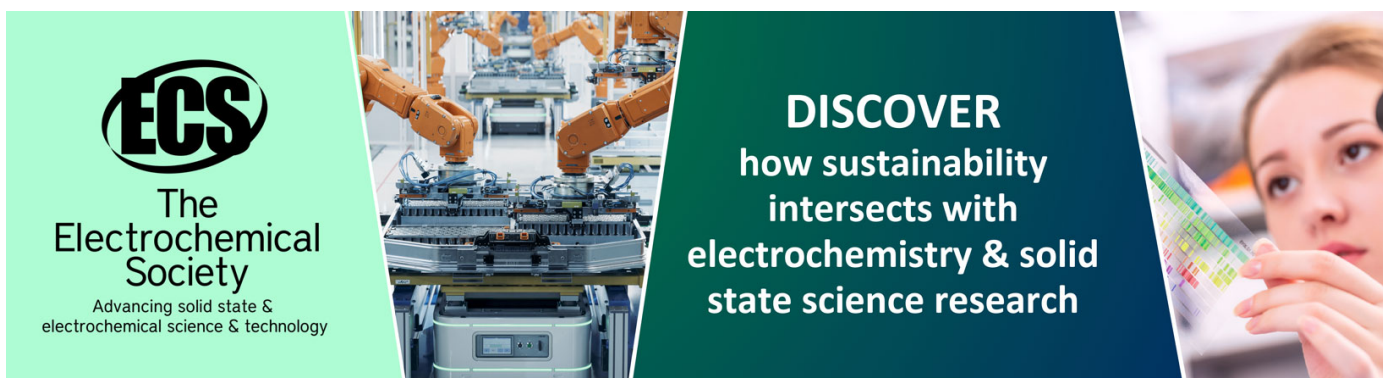
Dual roles of fulvic acid on the photodegradation of propranolol under different light-source irradiation

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Dual roles of fulvic acid on the photodegradation of propranolol under different light-source irradiation

N Peng¹, K F Wang^{1,*}, P P Liao¹ and W H Huang¹

¹ School of Chemistry and Environment, Jiaying University, Meizhou, 514015, China
kfwang11@163.com

ABSTRACT. The photodegradation behaviors of propranolol(PRO) in solutions containing fulvic acid were studied under different light source irradiation. PRO degraded fast by direct photolysis under UV-vis irradiation. The UV photolysis process of PRO involved the triplet state of PRO(³PRO*) and self-sensitization decomposition. Under simulated solar irradiation, PRO photodegraded fast through ³PRO* decomposition mainly. Under UV-vis irradiation, the PRO photodegradation was suppressed by SRFA and PLFA. Under simulated solar irradiation, SRFA and PLFA promoted PRO photolysis and the effects increased with increasing FA concentration. Compared with SRFA, PLFA owns higher reactive oxygen species (ROS) generation ability. SRFA and PLFA could suppress the reaction of PRO and ROS and the inhibition of SRFA is more significant than that of PLFA. This study demonstrates that DOM plays dual roles in the photodegradation of PRO acting as a sensitizer and quencher under different light source irradiation.

1. Introduction

A subclass of pharmaceuticals and personal care products (PPCPs), beta-blockers, have been widely detected in the environment in recent years (Ashton et al. 2004; Zuccato et al. 2005; Roberts et al. 2016). They have unknown and potentially serious consequences for aquatic ecosystems, including toxicity to algae (Johnson et al. 2007) and aquatic organisms (Owen et al. 2007). It is thus necessary to investigate the fates and behaviors of beta-blockers in aquatic systems. The presence of Dissolved organic matter (DOM) in natural waters played an important role in light-induced transformation pathways of organic contaminants. Sunlight irradiated DOM produces reactive oxygen species (ROS) such as singlet oxygen (¹O₂), hydroxyl radical (·OH) as well as excited triplet states of DOM(³DOM*) (Xu et al. 2011; Boreen et al. 2005; Semones et al. 2017). DOM may also play an opposite role and slow down the sunlight-induced transformation of PPCPs by various mechanisms (Janssen et al., 2014; Mangalgiri and Blaney, 2017). In this work, we investigated the light-source-dependent effects of DOM on PRO photolysis.

2. Experimental section

2.1. Chemicals

Propranolol hydrochloride (PRO, CAS:318-98-9, 99.0%), sorbic acid (SA, >99.0%), rose bengal (RB, >99%) and 2-acetonaphthone (2AN, >99%) were purchased from Sigma-Aldrich (USA). Standard DOMs were obtained from International Humic Substances Society (IHSS) (St. Paul, MN) including Suwannee River Fulvic Acid II (SRFA II) and Pony Lake Fulvic Acid (PLFA).

2.2. Photochemical experiments

Photochemical experiments were performed by a solar simulator (XPA-II, Xujiang) equipped with a 500-W xenon lamp. For UV-vis exposure, samples were irradiated in quartz-stoppered quartz glass tubes. For simulated solar exposure, samples were irradiated in glass-stoppered pyrex colorimetric tubes. For quenching experiments, aliquots of 65 mmol/L isopropanol solution, 20 mg/L NaN₃ and 0.18 mmol/L SA were added to quench $\cdot\text{OH}$, $^1\text{O}_2$ and $^3\text{PRO}^*$ respectively. Rose bengal, H₂O₂ and 2AN were added to PRO solution for studying the reaction of PRO with $^1\text{O}_2$, $\cdot\text{OH}$ and $^3\text{DOM}^*$ respectively.

2.3. HPLC analysis

The concentration of PRO was determined by HPLC. Shimadzu LC 20 was equipped with UV detector with a Hypersil ODS column (4.6 x 250 mm, 5 μm) chromatographic column.

The isocratic mobile phase was 30% acetonitrile and 70% 10 mmol/L phosphate buffer solution (pH 3.0). The flow rate was 1.0 mL/min and the detection wavelength was 213 nm.

3. Results and discussion

3.1. Direct photolysis

The effect of initial concentration on PRO photolysis in pure water under different light source irradiation is shown in Fig.1. The PRO photolysis followed pseudo-first-order kinetics under different light source irradiation. Under UV-vis irradiation ($\lambda > 200\text{nm}$), PRO photodegraded very quickly and the photolysis rates decreased with the initial concentration increasing. In contrast, PRO photodegraded slowly and the photolysis rates increased with the initial concentration increasing, when exposed to simulated solar irradiation ($\lambda > 290\text{nm}$) (Janssen et al., 2014).

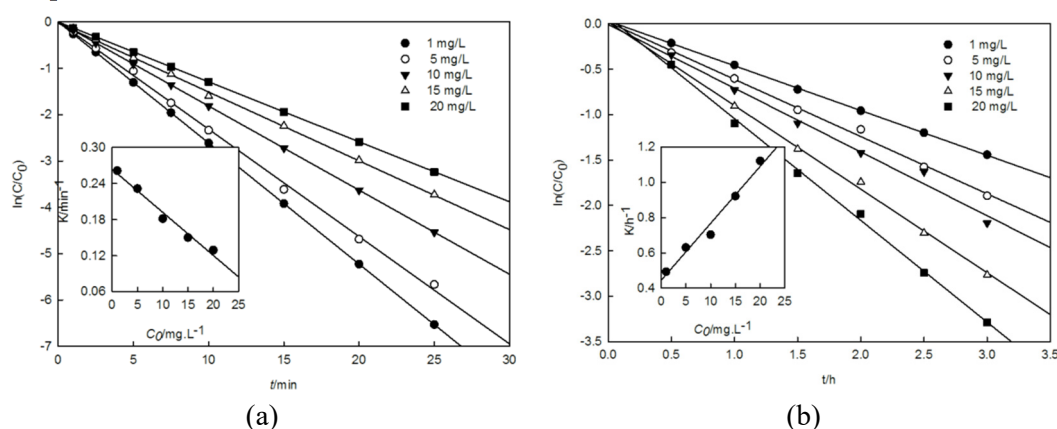


Fig.1 Effect of initial PRO concentration on photolysis kinetics in pure water at pH=7.0

(a) UV-vis irradiation (b) simulated solar irradiation

3.2. FA effects

The net differences in the observed pseudo-first-order rate constants for PRO photodegradation in the presence of SRFA and PLFA are shown in Fig.2. As shown in Fig.2, positive and negative differences implied sensitization and inhibition, respectively, of PRO degradation by FA. The observed rate constants for PRO showed different trends with FA type and light source condition. For example, Under UV-vis irradiation, the observed rate constant for PRO consistently decreased with increasing DOC for SRFA and PLFA. In contrast, PRO degradation was enhanced over the same DOC gradient under simulated solar irradiation. Though SRFA and PLFA showed similar net effect under the same light source irradiation, the differences were apparent between them. For example, under UV-vis irradiation, the inhibition of SRFA was greater than that of PLFA, while the sensitization of PLFA was stronger than that of SRFA under simulated solar irradiation.

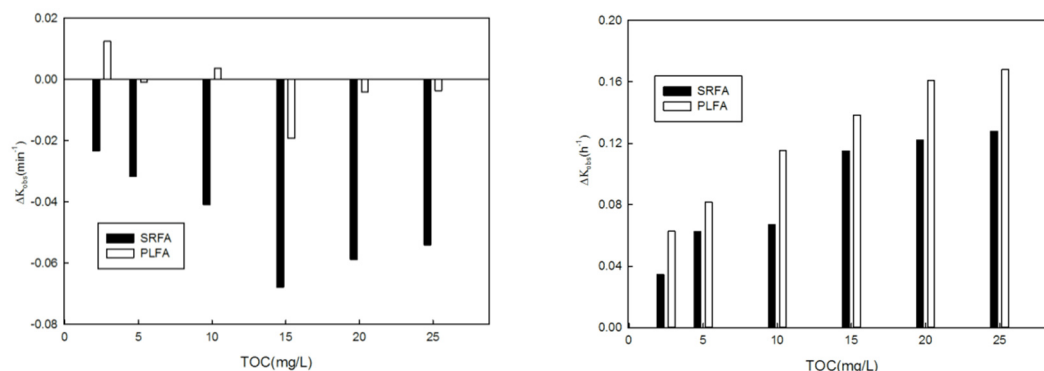


Fig.2 Effect of DOM source and concentration on the observed transformation kinetics of PRO(a) UV-vis irradiation (b)simulated solar irradiation

3.3. ROS generation

In order to explore the difference effect between SRFA and PLFA in the photolysis of PRO, the differences of ROS produced by two kinds of FA under simulated sunlight were studied(Fig.3).

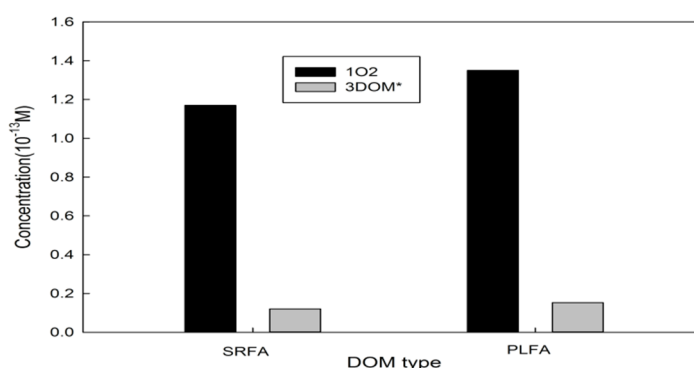


Fig.3 Steady state concentrations of $^1\text{O}_2$ and $^3\text{DOM}^*$ produced during irradiation of SRFA and PLFA solution

The $^1\text{O}_2$ concentrations were measured using the FFA probe compound ($k_{1\text{O}_2, \text{FFA}} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). For SRFA and PLFA, the steady state concentration of $^1\text{O}_2$ were 1.17×10^{-13} and $1.35 \times 10^{-13} \text{ M}$ respectively. The observed steady state concentrations of $^3\text{DOM}^*$ were determined using the TMP probe molecule ($k_{3\text{DOM}^*, \text{TMP}} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Like $^1\text{O}_2$, $^3\text{DOM}^*$ concentrations in PLFA solution is higher than that in SRFA solution. The steady state concentration of $^3\text{DOM}^*$ were 1.23×10^{-14} and $1.35 \times 10^{-14} \text{ M}$ respectively. These findings may be attributed to the greater presence of fulvic-like molecules in PLFA, as these compounds have been associated with greater steady state concentrations of $^3\text{DOM}^*$ and $^1\text{O}_2$.

3.4. Effects on reaction of PRO with ROS

Previous studies have reported suppression of PPCPs photolysis in the presence of DOM due to screening effects. However, we speculate the DOM effect on PRO photodegradation is related with the DOM effect on PRO oxidations induced by $^3\text{DOM}^*$, $^1\text{O}_2$ and $\cdot\text{OH}$. The use of 2AN, RB and H_2O_2 as model photosensitizers permitted verifying the enhancing and inhibiting effect of DOM. The results are shown in Fig.4.

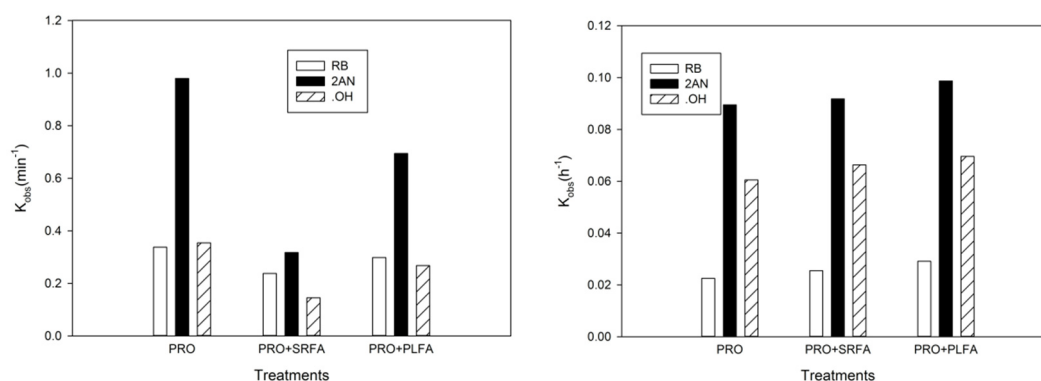


Fig.4 Effects of FA on the reaction between PRO and ROS (a) UV-vis irradiation
(b) simulated solar irradiation

As shown in Fig.4, under UV-vis irradiation, SRFA and PLFA inhibit the oxidation by the three ROS, and the strongest inhibition occurred in 2AN oxidation. Given the low reactivity of PRO with $^1\text{O}_2$ and $\cdot\text{OH}$, the oxidation induced by $^3\text{DOM}^*$ was the dominant photodegradation mechanism for PRO under UV-vis irradiation. Therefore, the inhibition of SRFA and PLFA is related to the quenching of reaction between PRO and $^3\text{DOM}^*$. Under simulated solar irradiation, SRFA and PLFA enhance the reaction between three ROS and PRO. Therefore, SRFA and PLFA enhanced the photodegradation of PRO.

4. Environmental implication

In this study, direct and indirect photolysis kinetics and mechanisms have been analyzed for PRO in the presence of SRFA and PLFA under different light source irradiation. While previous studies have described the DOM effect on PPCPs photodegradation is related with DOM composition, this study shows that DOM effects also due to the light source condition.

This study further identified the dual roles of DOM as both a sensitizer and quencher toward PRO degradation, depending on the light source conditions and the type of DOM.

Acknowledgments

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